Production and characterization of bio-oil from De-Oiled Cake

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By

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Certificate

This is to certify that the thesis entitled "Production and characterization of bio-oil from De-Oiled Cake" by Mr. Vivek Kumar Singh submitted to the National Institute of Technology, Rourkela for the Degree of Master of Technology is a record of bona-fide work, carried out by him in the Department of Chemical Engineering under my supervision. I believe that the thesis fulfils part of the requirements for the award of master of Technology. The results embodied in the thesis have not been submitted for the award of any other degree.

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Abstract

Linseed de-oil cakes, a source of biomass in the form of agriculture residue, could be an ideal source for the production of bio fuels that can be used as a substitute for the existing conventional fossil fuels which are at the verge of getting extinct. Though there are many biomass conversion processes like pyrolysis, combustion, gasification, liquefaction, hydrogenation, pyrolysis has gained special attention as it can convert biomass directly into solid, liquid and gaseous products by thermal decomposition in absence of oxygen. In this study linseed cake were pyro-lysed at a different temperature range of 350 ^{0}C to 600 ^{0}C with constant heating rate of 20 ^{0}C /min.

The maximum liquid yield obtained was 45.26% at a pyrolysis temperature of 525 ^{0}C for Linseed De-Oiled cake. The effect of temperature on pyrolysis of liquid product, char, and gaseous product were studied.

The various characteristics of liquid product obtained were identified on the basis of standard test methods. Effect of heating rate on the mass loss for all the raw materials were examined using the thermo gravimetric analysis profiles (TGA). The empirical formulas of the bio-oil with heating value were established. The chemical compositions of the bio-oils and char were investigated using FTIR, GC-MS. The fuel properties of the bio-oil such as kinematic viscosity, fire point, flash point, pour point, cloud point, and specific gravity were also determined. After further treatment the oil can be used as chemical feed stock.

Keywords: Linseed cake, pyrolysis, bio-oil, TGA, FTIR, GC-MS, etc.

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Abbreviations:

CHNS-Carbon, Hydrogen, Nitrogen, Sulphur

TGA- Thermo-Gravimetric Analysis

GCV- Gross Calorific Value

Chapter 1

Introduction

1. Introduction

1.1 Origin of the study

Energy crisis and environmental degradation is the main problem that mankind facing now a days. This is due to the growing population, rapid industrialization and disposal of diverse solid wastes, which are generated on a regular basis. To solve this energy crisis and environmental degradation, scientists are putting much effort on the potentials of utilizing appropriate technologies to recover energy and useful by-products from domestic and industrial solid wastes. Thus considerable research has been done to recover energy from waste material. Such materials include biomass, municipal solid wastes, industrial wastes, agricultural wastes and other low grade fuels as well as high energy density materials such as rubber and plastics.

Biomass, which contributes to one-seventh of the world-wide energy consumption and for as much as 43% of the energy consumption in some developing countries, has a great potential to be a renewable source and can be replaced with the conventional fossil fuels. Though there are many biomass conversion processes like pyrolysis, combustion, gasification, liquefaction, hydrogenation, pyrolysis has gained special attention as it can convert biomass directly into solid, liquid and gaseous products by thermal decomposition in absence of oxygen.

Renewable energy has become more and more important since that there was a growing concern about the limitations of fossil fuels. There is growing interest in biomass fuels and raw materials because of problems associated with climate change. The thermal decomposition reactions play a crucial role during several of the biomass utilization processes.

Thermo gravimetric analysis (TGA) is a high-precision method for the study of pyrolysis at low heating rates, under well-defined conditions in the kinetic regime. It can provide information about the partial processes and reaction kinetics. On the other hand, TGA can be employed only at relatively low heating rates because the true temperature of the samples may become unknown at high heating rates.

The socio economic development of any country mainly relies on independence and self-sufficiency in the energy fronts. In enhancing the energy options the current research and exploration in non-conventional energy technology involuntarily leads to efficient and

regulated utilization of the abundantly available natural renewable resource, the biomass. Pyrolysis is one of the key interesting and challenging area of research. Besides that, pyrolysis of linseed cake has several advantages that can help resolve the energy crisis. So a number of studies have been conducted to investigate the pyrolysis of linseed cake in both laboratory and industrial scale, under either inert or partial oxidizing atmosphere and maybe optimized to produce high energy density oils, solid char and gases. In addition to that, the oil products can be stored until required or readily transported to where it can be most efficiently utilized .And it is well-known that linseed cake has high volatiles and low ash content. So linseed cake can be a source of energy and valuable chemical product, and their thermal decomposition makes the recovery of useful compounds possible.

Table 1: Production of oil seed in India

Oil-Seeds	**Oil-Content**	**Production (Million Tons)**				
		2012-2013	**2011-2012**	**2010-2011**	**2009-2010**	**2008-2009**
Ground nut	35-40	6.12	5.80	6.94	4.35	6.50
Caster seed	45-50	0.92	0.98	0.95	0.79	0.91
Seesem seed	48-49	0.86	0.68	0.69	0.63	0.60
Mustered	42-45	6.02	6.79	4.69	6.20	6.77
Linseed	35-45	0.15	0.14	0.19	0.19	0.20
Niger seed	32-43	0.07	0.09	0.08	0.08	0.11
Safflower	30-45	0.14	0.18	0.18	0.20	0.21
Sunflower	39-49	0.98	1.16	1.47	1.61	1.62
Soybean	20-30	8.51	8.99	9.47	7.86	7.5
Neem	20-30	0.11	-	-	-	-
Mahua	33-40	0.17	-	-	-	-

Therefore in recent years there has been an increased interest in production of oil fuel from linseed cake by pyrolysis method. This innovative technology, because of its portability and scalability, uniquely address the challenges faced when converting linseed cake to low sulphur oil.

Biomass provides a clean, renewable energy source that could dramatically improve our environment, economy and energy security. Few of the advantages and benefits of biomass for energy usage are:

1.2. Abundance: availability of biomass is worldwide, which assures uninterrupted supply of Raw material to the energy unit.

1.3. Secure: a significant contributor to the national energy supply and will ensure economic Benefits along with greater autonomy and freedom from external resources.

1.3.1. Domestic Resource: not sensitive to world price fluctuations or the supply uncertainties of imported fuels.

1.3.2. Socio-economic: Development: creation of employment opportunities in rural areas.

Table 2: World population by region (millions)

Region/country	History			projection				average annual Percentage change,
	2005	2007	2008	2015	2020	2030	2035	2008-2035
OECD (Organization for Economic Cooperation and Development)								
OECD (North America)	431	435	440	476	499	522	546	0.6
North America	296	299	301	326	326	342	358	0.5
United States	031	032	032	035	037	039	041	0.6
Canada	102	103	104	113	119	124	129	2.8
Mexico	534	537	540	557	564	570	574	3.1
OECD (Europe)	199	199	200	202	201	200	198	2.2
OECD (Asia)	127	127	127	125	123	121	118	1.5
Japan	047	047	047	048	048	048	048	2.2
Australia and New Zealand	024	024	024	026	027	030	031	1.8
Total (OECD)	1,167	1,175	1,183	1,238	1,267	1,294	1,319	0.5

Chapter 2

Literature review

2. Literature review:

2.1. Biomass

Biomass is biological material derived from living, or recently living organisms. It most often refers to plants or plant-based materials which are specifically called ligno-cellulosic biomass. As an energy source, biomass can either be used directly via combustion to produce heat, or indirectly after converting it to various forms of biofuel.

Biomass mainly consists of cellulose, hemicelluloses, lignin, lipids, proteins, simple sugars and starches and among these compounds, cellulose, hemicelluloses, and lignin are the three main constituents. Conversion of biomass to biofuel can be achieved by different methods which are broadly classified into: thermal, chemical, and biochemical methods.

Table 3: Percentage of cellulose hemicellulose and lignin in biomass

Component	Percent Dry Weight	Description
Cellulose	40-60	cellulose is an organic compound with the linear formula $(C_6H_{10}O_5)_n$. Linear chain of glucose linked by b-glycosides linkage. This chain is stable and resistant to chemical attack.
Hemicellulose	20-40	It is known as polyose. Six carbon sugars such as D-galactose, D-glucose, and D-Mannose) and uronic Acid. Lower molecular weight than cellulose.
Lignin	10-25	A biopolymer rich in three dimensional, highly branched poly-phenol constituents that provide structural integrity to plants. Amorphous with no exact structure.

2.2 Why Biomass?

1. Biomass is renewable and available essential for all countries in the world and at any time.
2. Availability of Biomass is high.
3. Biomass contains negligible sulphur, nitrogen and metal contents hence it helps in Minimizing the acid rain.
4. It can help mitigate climate change, water pollution and soil erosion.
5. Valuation of wastes.
6. Fixation of rural population and depletion of fossil fuels.

2.3 Sources of Biomass

The main sources of biomass resource include agricultural crops, wood and wood wastes, and their waste by-products, municipal solid waste, animal wastes, waste from food processing and aquatic plants and algae.

2.4 Biomass Conversion Processes

The energy form biomass can be converted to useful forms by using a number of different processes. Factors that influence the choice of conversion process are:

Type and quantity of biomass feedstock

- Desired form of the energy i.e. end-use requirements
- Environmental standards
- Economic conditions;
- Project specific factors

In many situations it is the form in which the energy is required that determines the process route followed by the available types and quantities of biomass. Broadly they are classified into two types. Figure. 1 shows the block diagram of various conversion process and uses of their products.

De-oiled cake, which is one of the forms of agricultural residue, could be a potential source of raw material for extraction of bio fuels. The most effective way of extraction of bio fuels from

these de-oiled cakes is pyrolysis and the literatures of the work carried out on these cakes, residues of their trans-esterified bio-oils derived from seed are given below.

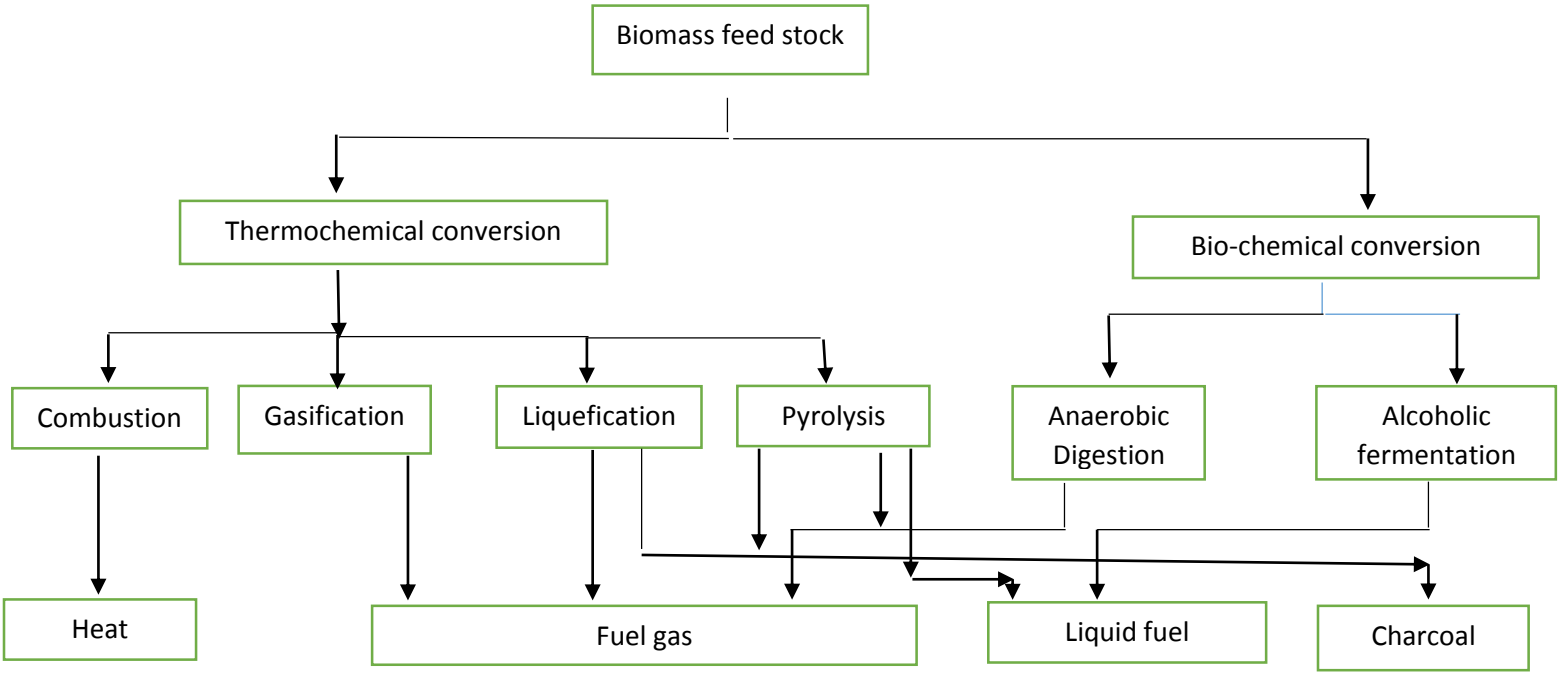


Figure 1: Biomass Feed Stock Conversion by Different Method

They are

1. Thermo chemical processes

2. Bio-chemical processes

Thermo-chemical conversion is classified into four processes. They are

1. Combustion

2. Gasification

3. Liquefaction

4. Pyrolysis

2.4.1 Combustion

Combustion is an exothermic chemical reaction accompanied by large heat generation and luminescence. In this process biomass is directly burnt in the presence of air to convert chemical energy into heat, mechanical power, or electricity, etc. Combustion proceeds by gas phase reaction, surface reaction or both following processes such as fusion, evaporation, mixture, diffuse, convection, heat conduction, radiation complexly at high velocity. It is possible to burn any type of biomass but in practice combustion is feasible only for biomass with moisture content less than 50%. Combustion of biomass produces hot gases at temperatures around 800 ^{0}C - 1000 ^{0}C that can directly be used for the production of electricity. Wood or woody biomass burns to carbon dioxide

(CO_2) and water vapour (H_2O) as follows

$$C_{42}H_{60}O_{28} + 43O_2 \longrightarrow 42CO_2 + H_2O$$

Many countries are using biomass by burning it as fuel to generate heat. According to a general rule, though complete combustion is impossible, combustion requires the three T's, meaning sufficiently high temperature, strong turbulence of the air as mixture, and a long residence time of the mixture in the fire chamber. Turbulence and long residence time bring each pyro-lysis gas molecule close to oxygen and provide chances for more combustion. This combustion proceeds in many intermediate steps and with the various wood pyrolysis products on different routes.

2.4.2 Gasification

Gasification is the conversion of biomass into a combustible gas mixture by the partial oxidation of biomass at high temperatures, typically in the range 800 ^{0}C – 900 0C. Air gasification is the most widely used technology since a single product is formed at high efficiency. And without requiring oxygen. Either air, oxygen enriched air or oxygen may be used with steam added as a reagent and/or temperature control medium. Raw materials are mainly wood chips and corn stalks. The low calorific value (CV) gas produced (about 4–6 MJ/Nm^3) can be burnt directly or used as a fuel for gas engines and gas turbines. The product gas can be used as a feedstock (syngas) in the production of chemicals (e.g. ethanol). The biomass is heated in insufficient supply of air.

The reactions are as follows:

$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$

$C + O_2 \longrightarrow CO2$

$C + O_2 \longrightarrow CO$

$CO + 1/2O_2 \longrightarrow CO_2$

$CO_2 + C \longrightarrow CO_2$

Methane and hydrogen are also formed simultaneously by thermal splitting of organic material. In recent years, many attempts have been made to gasify cellulosic materials, such as cotton, wood, bark, peat and rice hulls. One promising concept is the biomass integrated gasification/combined cycle, where gas turbines convert the gaseous fuel to electricity with a high overall conversion efficiency.

2.4.3 Liquefaction

Liquefaction process converts biomass into liquid oils, hydrogen, bio fuels, synthesis gas, bio chemicals and alcohols. Liquefaction process can treat high moisture content biomass. Liquefaction can be accomplished directly or indirectly. Direct liquefaction, is a low-temperature and high pressure process in which biomass is broken down into fragments of small molecules in water or another suitable solvent. Lignocelluloses biomass materials are the most widely used types of biomass for bio-oil production through liquefaction. In liquefaction process, biomass undergoes de-polymerization and is decomposed into monomer units. These monomer units, however, may be re-polymerized or condensed into solid chars, which are undesirable.

A solvent is generally added to slow down the higher order solid-state reactions, thus reducing the detrimental condensation reactions. The use of catalysts is a critical factor in biomass liquefaction as it can reduce the required reaction temperature, enhance reaction kinetics, and improve the yield of desired products. Indirect liquefaction of biomass is accomplished by first

gasifying it to produce a synthesis gas consisting of hydrogen and oxides of carbon, which in turn are converted to any one of a number of liquid fuels and chemicals by suitable choice of catalyst, synthesis gas composition and reaction conditions. This approach to producing synthesis fuels and chemicals has been extensively investigated that the carbonaceous feed material, but less for biomass or other Feed stocks.

2.4.4 Pyrolysis

Amongst the thermo-chemical processes, pyrolysis has received increasing attention because they produce high energy pyro-lytic oils in addition to char and gas. Pyrolysis is a thermal decomposition process that takes place in the absence of oxygen to convert biomass into solid charcoal, liquid (bio-oil), and gases at higher temperatures. Pyrolysis processes are of three types. They are

1. Slow or Conventional pyrolysis

2. Fast Pyrolysis

3. Flash Pyrolysis

Conventional or slow pyrolysis process, are done at relatively long vapour residence time (minutes to days), at low heating rate (3- 5 ^{0}C/min) and moderate temperatures of around 300 - 400 ^{0}C. This process is mostly used to maximize char yield which increases up to 30% when compared to other processes.

Fast pyrolysis is a pyrolysis process occurring at high heating rate (as high as 50 - 100 ^{0}C/min), Short residence time (minutes to seconds) and higher temperatures of around 450- 600 ^{0}C. It particularly favours the formation of liquid products, but inhibits the formation of solid chars. Bio-oil, the major product from fast pyrolysis, is a potential liquid fuel that bio-oil derived from wood pyrolysis.

Flash pyrolysis is a pyrolysis process occurring at relatively high temperatures of above 700°C; at very high heating rates and similarly short residence times. It particularly maximizes gas yields with minimum liquid and char production.

2.5 Bio-Mass and Its Future Uses

In the future, biomass has a great potential to provide a cost effective and sustainable supply of energy and helping reduce greenhouse emissions.

1. By the year 2050, it is projected that 90% of the world population will live in developing countries and there is an urgent need that all the biomass processes used are sustainable and energy efficient.

2. Usage of advance technologies by which there is an increase in more efficiency of biomass manufacture and conversion, might be one possible reason for the increased usage of Biomass.

3. Biomass waste and residues are expected increase and can be substituted by energy crops in The elongated term.

4. The success of the biomass derived chemicals industry will depend on the supply and Demand for feedstock, primary chemicals and key intermediates the petrochemical industry Cannot create, such as cellulose and lactic acid.

5. Electricity generation lies in biomass integrated by gasification/gas turbine technology, which offers high energy conversion efficiencies.

2.4.5 Biochemical Processes

The process of bio-chemical conversion of biomass carried out by two main processes.

They are,

1. Alcoholic fermentation

2. Anaerobic digestion or fermentation, for producing biogas.

2.4.5.1 Alcoholic Fermentation

The main products of this process are liquid fuel like ethanol that is produced by the process of fermentation from biomass materials which consist of sugars, starch or cellulose provides a high quality fuel for storage and transport. It should be noted that the biochemical conversion of woody wastes is more difficult for the fermentative degradation and need first to be broken down by acidic or enzymatic hydrolysis because of the presence of longer-chain polysaccharides.

On the basis of energy utilization, product ethanol after distillation purification can be used as a supplement or substitute for petrol or gasoline in cars. Also, biomass materials for alcoholic fermentation are generally agricultural production/processing residues or energy crops. Molasses, a by-product of sugar-manufacturing process, has been industrially bio-converted for the production of ethanol.

2.4.5.2 Anaerobic Digestion

Anaerobic digestion is the conversion or degradation of organic wastes through microbial actions in the absence of oxygen to reducing gases (biogas) that mainly consist of methane and carbon dioxide and contain various trace components such as hydrogen sulphide, acids and thiols. A typical example is the landfill gas (LFG) from the MSW buried in sanitary landfill sites. The collected LFG, which generally consists of up to 50% methane, can be purified and then burned in engines or turbines to produce heat and electricity.

Practically, the biogas is commonly produced by using animal manure in an airtight container (digester). Due to the high heating value (5400–6000 kcal/Nm^3) of biogas, the biogas thus generated can be directly combusted in burners for cooking, or used as gas fuel in internal combustion engines to generate electricity, or further upgraded to natural gas quality by the removal of carbon dioxide and hydrogen sulphide.

Table 4: Characterization of chemistry and products of biomass pyrolysis

Type	Feature and Process	Products and their characterizations
Pyrolysis of holocellulose	**General effect:** Colour changes from brown to black lexibility and mechanical strength are lost, size reduced, weight reduced. **Processes:** **Dehydration**: also known as char forming reactions produces volatile products and char. **Depolymerisation** : produces tar **Effect of temperature**: At low temperatures dehydration pre-dominates, at 630K depolymerisation with production of levoglucosan dominates. Between 550 and 675K products formed are independent of temperature.	**Volatile product**s: Readily escape during pyrolysis process, 59 compounds are produced out of which 37 have been identified CO, CO_2, H_2O, acetyl, furfural, aldehydes, ketones. **Tar:** Levoglucosan is principal component. **Char**: As heating continues there is 80% loss of weight and remaining cellulose is converted to char, prolonged heating or exposure to higher temperature (900K) reduces char formation to 9 %.

Pyrolysis of lignin	**Conventional (Carbonization):** At 375-450 K endothermic reaction From 675 K exothermic reaction Maximum rate occurring between 625 and 725 K. **Fast and Flash pyrolysis**: High temperature of 750K, rapid heating rate finely ground material, less than 10% moisture content, rapid cooling and condensation of gases, yields in 80% range, char and gas used for fuel	**Char:** approximately 55% **Distillates:** 20%, methanol, methoxyl groups, acetone acetic acid **Tar:** 15%, phenolic compounds and carboxylic acid **Gases:** CO, methane, CO2, ethane **Bio-oil**: will not mix with hydrocarbon liquids, cannot be distilled, substitute for fuel oil and diesel in boilers, furnaces, engines, turbines, etc. **Phenols:** utilizes a solvent extraction process to recover phenolic and neutrals, 18-20% of wood weight, secondary processing of phenol pharm aldehyde resins, adhesives, injection molded plastics.

2.6 Literature in De-Oiled Cakes

F. Karaosmanoglu et. al., conducted slow pyrolysis experiments on straw and stalk of the Rapeseed plant in a tubular reactor under the conditions of static atmosphere, varying temperatures of 350 ^{0} C, 450 ^{0}C, 550 ^{0}C and 650 ^{0}C and at heating rates of 10 ^{0}C min^{-1} and 30 ^{0}C min^{-1}. The maximum liquid yield was observed to be evolving at 650 ^{0}C pyrolysis temperature and at a heating rate of 30 ^{0}C min^{-1}. S. Ucar et. al., investigated the composition of products from the pyrolysis of rapeseed oil cake in a fixed bed reactor at 400 0C, 450 0C, 500 0C, 700 0C and 900 0C at a heating rate of 5 0C min-1 in nitrogen atmosphere. The maximum oil yield was obtained at a temperature of 550 0C. K. Giannakopoulou et. al. studied on the method for the development of catalytic conversion of biomass into liquid products and their characterization in a batch and fixed bed reactor. Rapeseed cake was used as raw material, while H-ZSM-5 and H-Beta zeolites were used as catalysts. They concluded that addition of catalysts in the conversion system reduced the liquid phase yield compared to the non-catalytic processes. K. Giannakopoulou et. al. used H-ZSM-5, Fe-ZSM-5 and H-Beta, zeolite catalysts of three types to study the catalytic co-conversion of rapeseed cake and safflower oil under low pressure, at the temperatures of 350, 400 0C a heating rate of 6 0C/min. The liquid phase characteristics varied by the use of different catalysts. **N. Ozbay et. al.,** conducted fixed bed pyrolysis experiment is two kind of reactors namely tubular and a Heinze to study the effect of temperature on yields and chemical composition of products. The maximum oil yield of 29.68% was obtained in N2 atmosphere at a pyrolysis temperature of 550°C with a heating rate of 7°C min -1 in a tubular reactor.

Chapter 3

Materials and method

3. Materials & Methods

3.1 Raw material

The linseed de-oiled cake used in the experiment was brought from a fodder shop from a local market of Rourkela, Orissa, India. The cake was in the form of flaks, and was powdered, using a household grinder, before use so as to minimize void inside the reactor as well as to fill maximum amount of cake in to the reactor.

3.2 Characterization:

3.2.1 Proximate and Ultimate Analysis:

The proximate analysis was done by **ASTM D3173-75.** The ultimate analysis was done by using Elementor **CHNS analyser**. Calorific value of the raw material was found by ASTM D5868-10a.

3.2.2 TGA

TGA analysis of the sesame/neem/mustard/mahua cake was done by using **SHIMADZU** TGA-60H with nitrogen as carrier gas at a constant flow rate of 45 ml/min.

3.2.3 FTIR

The pyro lytic oil obtained was analysed for its functional by using **PERKIN ELMER RX.** The **FTIR** spectra were collected in the range of 400-4000 cm^{-1} region with 8cm-1 resolution.

3.2.4 GC-MS

Pyro lytic oil obtained was characterized by using **GC/MS- QP 2010 SHIMADZU**, Equipped with flame ionization and mass spectrometry detection (**GC-FID-MS**).

Table 5: Standard Methods for Physical Property Analysis

Physical Property	Method
Specific gravity	I.S:1448 P:16
Density	I.S:1448 P:16
Kinematic viscosity	I.S:1448 P:25
Conradson carbon Residue	I.S:1448 P:122
Flash point by Abel Method	I.S:1448 P:20
Fire point	I.S:1448 P:20
Cloud Point	I.S:1448 P:10
Pour point	IS:1448 P:10
Gross Calorific Value	IS:1448 P:6
Sulphur Content	IS:1448 P:33
Cetane Index	IS:1448 P:9
Distillation Boiling Range	IS:1448 P:18

3.3 TGA (Thermo-gravimetric analysis)

3.3.1 Kinetic Modelling

Biomass pyrolysis involves numerous extremely complex reactions and end up with large number of intermediates and end products, devising an exact reaction mechanism and kinetic modelling for biomass pyrolysis is extremely difficult, hence, pyrolysis models are modelled on the basis of visible kinetics.

Thus, pyrolysis kinetic modelling paved the way for researchers to propose different reaction schemes in different times; in due course this has developed a long history. Hence even today it is difficult to develop a precise kinetic model taking into account all the parameters concerned. Revisiting the mechanisms for pyrolysis of biomass so far developed reveals a general approach: virgin biomass as the raw material and with gas / volatiles, tar, char as the end products.

Table 6: Methods for studying solid-state kinetics

Model-fitting		Model-free	
Isothermal	**Non-isothermal**	**Isothermal**	**Non-isothermal**
– Conventional	– Differential	– Standard	– Kissinger
	– Freeman –Carroll	– Friedman	– Flynn–Wall an Ozawa
	– Coats–Redfern	– AIC	– Vyazovkin and AIC
			–Kissinger–Akahira–Sonuse

Thermal behaviour of linseed cake can be improved by knowing thermal degradation kinetics. So the kinetic study of linseed cake pyrolysis provides a useful basis upon which to design a pyrolysis reactor. A thermo-gravimetric analysis (TGA) technique is an excellent way for studying the kinetics of thermal degradation. It provides information on pre-exponential factor and activation energy. When these polymeric materials subjected to heating or burning conditions, complicated reaction mechanism such as random-chain scission, end- scission, chain stripping, cross-linking and coke formation take place.

The mechanisms of pyrolysis include a wide range of different reactions. Not every reaction causes the release of a volatile molecule. Some only cause a change in mechanical properties. During thermo-gravimetric analysis, only the weight loss is measured on heating, that means only those reactions causing the weight loss are considered. Furthermore, because of the system complexity, all reactions are lumped together into an overall reaction.

3.3.2 Kinetic theory

The one-step global model assumes that the de-volatilization phenomena proceeds as a single reaction

$$\textbf{Biomass} \xrightarrow{k} \textbf{Volatile + Char}$$

Where volatiles means the sum of the gas and tar and k is defined as the rate constant of reaction whose temperature dependence is expressed by the Arrhenius equation

$$\textbf{Volatile = Gas + Tar}$$

$$K = Ae^{-E_a/RT}$$

$$\ln K = \ln A - \frac{E_a}{RT}$$

$\boldsymbol{E_a}$=Activation energy

T = Absolute temperature (K)

R = Gas constant (8.314 J/K mole)

A = Pre-exponential factor (min^{-1})

K = Rate constant

The rate of transformation from solid state to volatile product is given by following equation

$$\frac{d\alpha}{dt} = K(T)f(\alpha)$$

$$\alpha = \frac{W_0 - W_a}{W_0 - W_f}$$

α = conversion factor

$\boldsymbol{W_0}$= Initial Weight

$\boldsymbol{W_a}$= Actual Weight at time (t)

$\boldsymbol{W_f}$= Final Weight

The functional form of model $f(\alpha)$ is assumed to be the n^{th} order of the unreacted material according to following equation

$$f(\alpha) = (1-\alpha)^n$$

The rate equation for conversion factor in terms of the reaction rate constant K is

$$\frac{d\alpha}{dt} = K(1-\alpha)^n$$

$$\ln\frac{d\alpha}{dt} = \ln K + n\ln(1-\alpha)$$

For non-isothermal TGA experiments at linear heating rate

β = [dT/dt]

$$\frac{d\alpha}{dt} = \frac{A}{\beta}[e^{(-Ea/RT)}\ (1-\alpha)^n]$$

$$\frac{d\alpha}{(1-\alpha)n} = \frac{A}{\beta}[e^{(-Ea/RT)}dt]$$

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)n} = \int_0^{T} \frac{A}{\beta}[e^{(-Ea/RT)}\ dt]$$

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)n} = \frac{A}{\beta}\int_0^{T}[e^{(-Ea/RT)}\ dt]$$

The right hand side of this equation cannot be integrated directly because the integral known as the temperature integral

$$\mathbf{I(u)}=\int_0^{T}[e^{(-Ea/RT)}\ dt]$$

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)n} = \frac{A}{\beta} * I(u)$$

Put $(1-\alpha)$ = p

Then after differentiation

-dα = dp

Put it in above equation

$$\int_0^{\alpha} \frac{-dp}{p^n} = \frac{A}{\beta} * I\,(u)$$

$$\frac{-P^{-n+1}}{(-n+1)} = \frac{A}{\beta} * I(u)$$

$$\frac{1-(1-\alpha)^{-n+1}}{(-n+1)} = \frac{A}{\beta} * I(u)$$

u= E/RT

$$\mathbf{I(u)}=\int_u^{\infty} \frac{e^{-u}}{u^2}\ du$$

$$\int_0^{T} e^{-(\frac{E}{RT})} dT = \frac{RT^2}{E} e^{-(\frac{E}{RT})} Q(u)$$

where Q(u) is the function which changes slowly with u and is close to unity.

$$\mathbf{I\ (u)} = \frac{e^{-u}}{u^2} Q(u)$$

$$\mathbf{g(\alpha)}=\frac{AR}{\beta E} T^2 e^{-\frac{E}{RT}} Q(u)$$

That is the starting equation for many integral methods of evaluating non-isothermal kinetic parameters:

This equation expresses the fraction of material consumed in the time. In this work the activation energy was obtained from non-isothermal TGA. The methods used to calculate kinetic parameters are called model-free non-isothermal methods and require a set of experimental tests at different heating rates.

$$\frac{\mathbf{1-(1-\alpha)^{-n+1}}}{\mathbf{(-n+1)}} = \frac{\mathbf{A}}{\boldsymbol{\beta}} * \boldsymbol{I(u)}$$

Table 1. Expressions for Some Proposed Approximations for the Temperature Integral

Author	$\int_0^T e^{-(E/RT)}dT$	$P(u)$
Coats-Redfern[11]	$\frac{RT^2}{E}\left(1-\frac{2RT}{E}\right)e^{-(E/RT)}$	$\frac{e^{-u}}{u^2}\left(1-\frac{2}{u}\right)$
Gorbachev-Lee-Beck[12,13]	$\frac{RT^2}{E+2RT}e^{-(E/RT)}$	$\frac{e^{-u}}{u}\frac{1}{u+2}$
Li Chung-Hsiung[14]	$\frac{RT^2}{E}\left[\frac{1-2\left(\frac{RT}{E}\right)}{1-6\left(\frac{RT}{E}\right)^2}\right]e^{-(E/RT)}$	$\frac{e^{-u}}{u^2}\left(1-\frac{2}{u}\right)\Big/\left(1-\frac{6}{u^2}\right)$
Agrawal[15]	$\frac{RT^2}{E}\left[\frac{1-2\left(\frac{RT}{E}\right)}{1-5\left(\frac{RT}{E}\right)^2}\right]e^{-(E/RT)}$	$\frac{e^{-u}}{u^2}\left(1-\frac{2}{u}\right)\Big/\left(1-\frac{5}{u^2}\right)$
Quanyin-Su[16]	$\frac{RT^2}{E}\left[\frac{1-2\left(\frac{RT}{E}\right)}{1-4.6\left(\frac{RT}{E}\right)^2}\right]e^{-(E/RT)}$	$\frac{e^{-u}}{u^2}\left(1-\frac{2}{u}\right)\Big/\left(1-\frac{4.6}{u^2}\right)$
Wanjun-Yumen[17]	$\frac{RT^2}{1.00198882E+1.87391198RT}e^{-(E/RT)}$	$\frac{e^{-u}}{u}\frac{1}{1.00198882u+1.87391198}$
New equation	$\frac{RT^2}{E}\frac{E+0.66691RT}{E+2.64943RT}e^{-(E/RT)}$	$\frac{e^{-u}}{u^2}\frac{u+0.66691}{u+2.64943}$

$$\frac{\mathbf{1-(1-\alpha)^{-n+1}}}{\mathbf{(-n+1)}} = \frac{\boldsymbol{ART^2}}{\boldsymbol{\beta E}}\boldsymbol{e^{-\left(\frac{E}{RT}\right)}Q(u)}$$

$$\frac{\mathbf{1-(1-\alpha)^{-n+1}}}{\mathbf{(-n+1)T^2}} = \frac{\boldsymbol{AR}}{\boldsymbol{\beta E}}\boldsymbol{e^{-\left(\frac{E}{RT}\right)}Q(u)}$$

After taking logarithms on both side it will give

$$ln\frac{1-(1-\alpha)^{-n+1}}{(-n+1)T^2} = ln\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right) - \frac{E}{RT}$$

Q(u) = $\left(1-\frac{2RT}{E}\right)$ This is for $\mathbf{n \neq 1}$

When **n=1**

$$\ln \ln \frac{1}{1-\alpha} - 2\,ln\,T = ln\,\frac{AR}{\beta E}\left(1-\frac{2RT}{AE}\right) - \frac{E}{RT}$$

At room temperature, 2RT is about 5 KJ/ mole so that for most reaction

E >> 2RT

And the term

$\ln\frac{RT}{\beta E}\left(1-\frac{2RT}{E}\right)$ is treated as a constant .therefore , the rate equation have the form of a liner relationship when left hand side plotted against 1/T.

Chapter 4

Experimental setup

4. Experimental setup

4.1.1 Pyrolysis Procedure

The experiment was conducted in a reactor-furnace system in which the furnace temperature is maintained constant using a PID controller. The outlet of reactor was attached to a condenser to condense the vapours coming out of it and was collected in a collecting jar at the end of condenser. The seed sample was filled in a reactor of 300 ml and the reactor was kept in the furnace for heating at constant temperature. When the reaction starts, vapours coming out of reactor through the provided outlet are condensed in a condenser as shown in Fig. 2. Water is used as cooling medium in the condenser and circulated via a pump. The condensed vapours are collected in a container as the liquid product whereas there is some amount of non-condensable Gases which are simply left out. The liquid product collected contains oily water and bio-oil. Oil water is basically water with some dissolved hydrocarbons. Oily-water and bio-oil is further separated by difference in their density in a decanter.

Experimental setup:

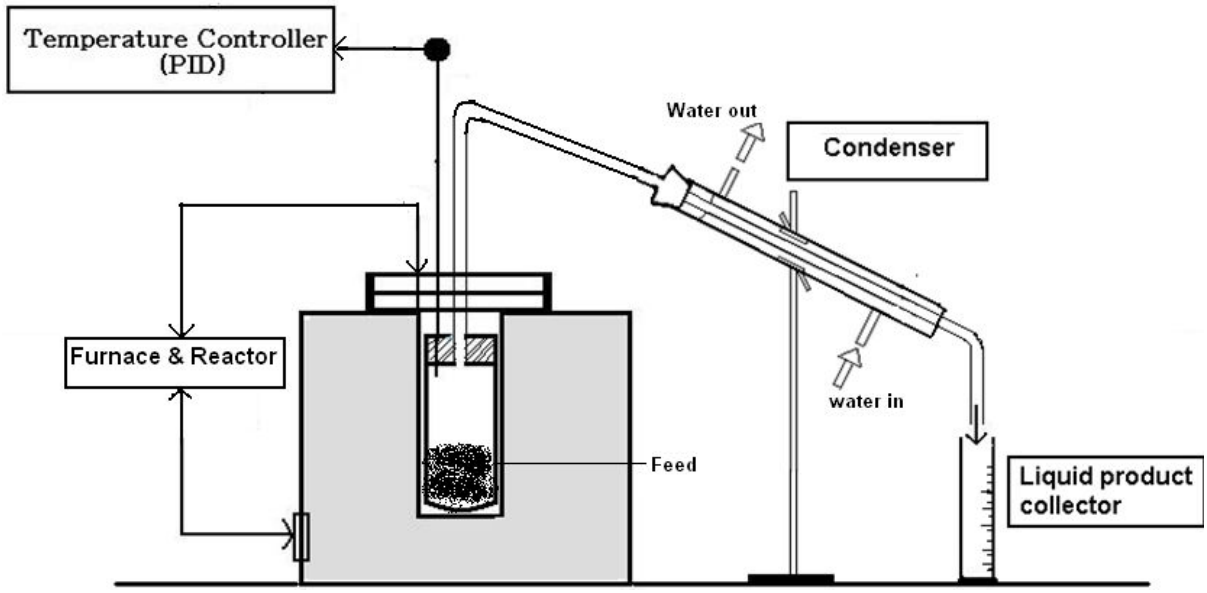


Figure 2: experimental setup for pyrolysis of linseed de-oiled cake

4.1.2 Semi-Batch Pyrolysis Reactor

Semi-batch pyrolysis reactor which was made of stainless steel (SS) (length- 16.5cm, 4.7 cm Internal diameter and outer diameter- 5.0 cm) sealed at one end and an outlet tube at other end.

Figure 3: Semi Batch Reactor

4.1.3 Sample Pyrolysis Run

Once the temperature range was established from the TGA curve then sample pyrolysis runs were done with 30 gm of seed in that range at intervals of 50 °C to determine the temperature at which maximum yield of liquid product is obtained. Various data like reaction time, yield of char, and yield of liquid product were noted down during sample runs. Variation in yield of char, liquid product and gas (volatiles) with respect to temperature is studied.

4.2 Experimental setup for TGA analysis

The thermo gravimetric system for decomposition studies is shown schematically in Fig. It consists of an electrically heated reaction tube of 18mm in inner diameter and 165mm in length. About 9mg of the sample was placed in a quartz cell of 6mm in diameter. The cell was then put on a platinum crucible, hung by a 155mm long suspension wire, and connected to the thermo balance.

The temperature of reaction tube is 373–1273K and is controlled by a type-K chrome–alumel thermocouple wire placed about 1–2mm below the platinum crucible. The heating rate of the reaction tube can be pre-set manually in the range of 0–99 K/min. In this study, heating rates β = 10, 15, and 20 K/min were chosen. The carrier gas passed through the reaction tube from top to bottom and volatile products were collected by a water trapper. Note that in order to obtain the intrinsic reaction rate, the effects of heat transfer and temperature gradient in the sample should be eliminated. The heat transfer effect can be reduced by purging carrier gas velocity as high as possible. As such, flow rate of nitrogen gas was supplied at 50 ml/min for all the tests. In addition, two methods might be used to reduce any error in temperature measurement due to temperature gradient: bring the thermocouple in contact with the sample or reduce the sample size. As pointed out by Antal et al, the first method is not usually possible with a thermo-gravimetric apparatus.

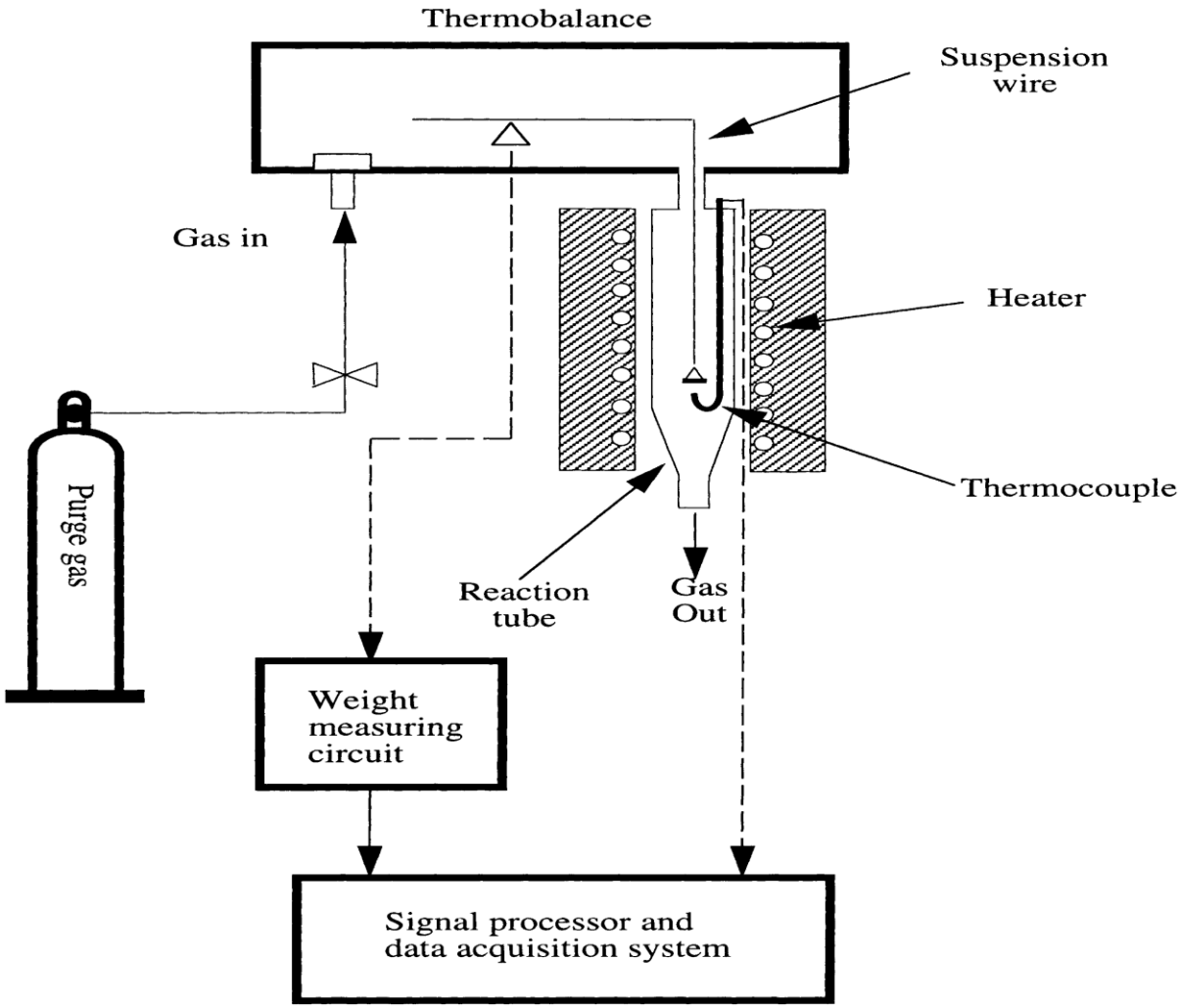


Figure 4: Experimental setup for TGA analysis

4.3 Shoxlet apparatus

Normally a solid material containing some of the desired compound is placed inside a thimble made from thick filter paper, which is loaded into the main chamber of the Soxhlet extractor. The extraction solvent to be used is taken into a distillation flask and the Soxhlet extractor is now placed onto this flask. The Soxhlet is then equipped with a condenser.

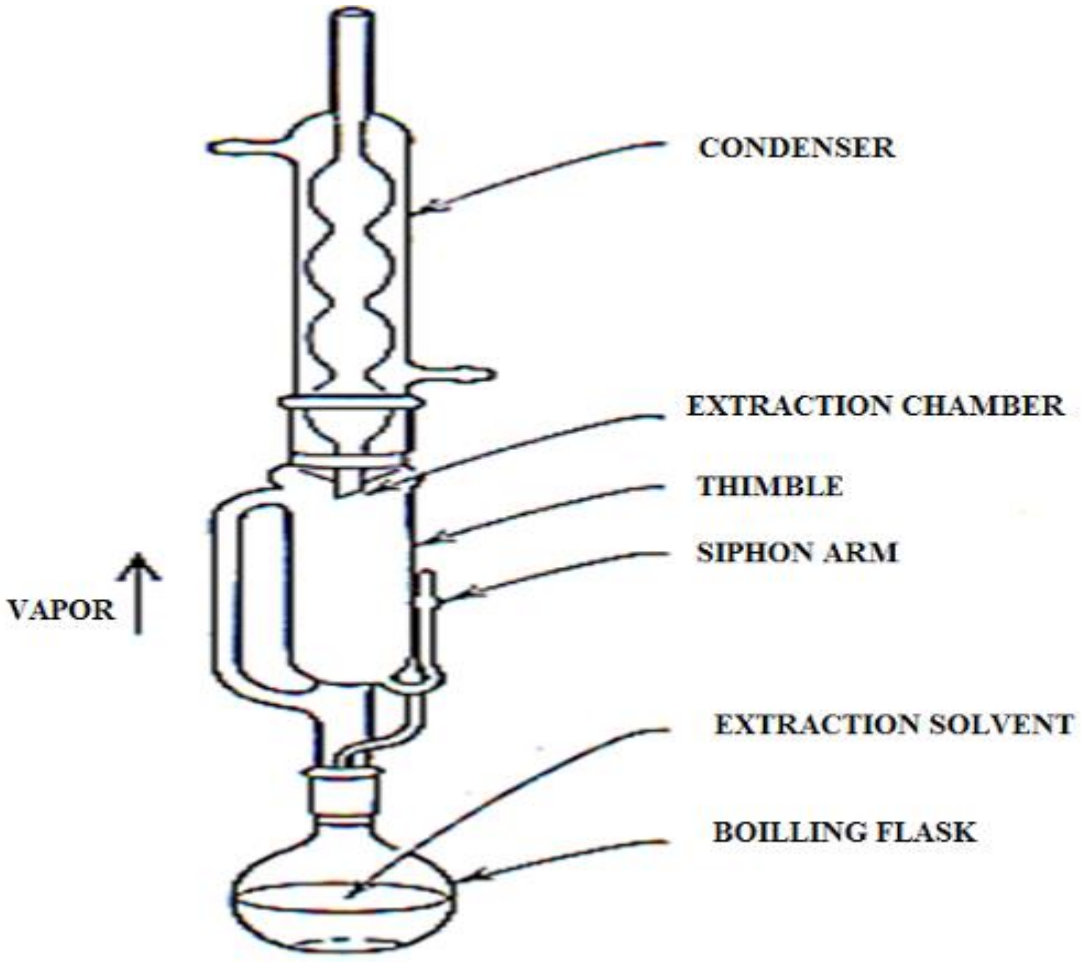


Figure 5: soxhlet apparatus

The solvent is heated to reflux. The solvent vapour travels up a distillation arm, and floods into the chamber housing the thimble of solid. The condenser ensures that any solvent vapour cools, and drips back down into the chamber housing the solid material. The chamber containing the solid material is slowly filled with warm solvent. Some of the desired compound will then dissolve in the warm solvent.

When the Soxhlet chamber is almost full, the chamber is automatically emptied by a siphon side arm, with the solvent running back down to the distillation flask. The thimble ensures that the rapid motion of the solvent does not transport any solid material to the still pot. This cycle may be allowed to repeat many times, over hours or days.

During each cycle, a portion of the non-volatile compound dissolves in the solvent. After many cycles the desired compound is concentrated in the distillation flask. The advantage of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled.

After extraction the solvent is removed, typically by means of a rotary evaporator, yielding the extracted compound. The non-soluble portion of the extracted solid remains in the thimble, and is usually discarded.

Chapter 5

Results and discussion

5. Results and discussion

5.1 Proximate and ultimate analysis of raw material

Proximate was done by ASTM D3173-75 and elemental analysis was done by using elemental CHNS analyser. Calorific value of the raw material was found by ASTM D5868-10a.The samples such as linseed cake was identified with the following characteristics using proximate and ultimate analysis. Table 3 gives an idea for thermal degradation of the sample showing more volatile content along with moderate fixed carbon composition.

Table 8: Proximate and ultimate analysis of Linseed De-Oiled Cake

Type of used raw material	**linseed cake**
Proximate analysis	
Moisture content	10.0
Volatile content	68.0
Fixed carbon	17.20
Ash content	4.8
C	42.80
H	5.20
N	4.79
S	0.70
O	46.51
C/H molar ratio	0.68
C/N molar ratio	10.42
% oil content	19.65
Empirical formula	$C_{0.68}HN_{0.07}S_{0.004}O_{0.55}$
Calorific Value (cal /gm)	4912

5.2 Pyro-lytic yield of linseed de-oiled cake

The TGA analysis of the biomass samples were done prior to pyrolysis which conferred that the degradation temperature of the biomass & the temperature for the biomass pyrolysis has gained he knowledge & according as the pyrolysis of the biomass was done in order to get the

desired products in 3 forms i.e., the liquid product as bio-oil, the solid product as bio-char & at last the volatiles. The biomass proximate analysis was conducted which revealed a high moisture content was high hence the sample was first sieved to a size & then dried in the oven for 12 hours. The bio-oil obtained from pyrolysis was analysed for their further use firstly the yield was studied of bio-oil , bio-char and gas content with respect to temperature at various pyro-lytic temperatures starting from 350- 600 ^{0}C .

Table 9: Conversion of linseed de-oiled cake With Temperature in Semi Batch Reactor

Temperature	Total liquid %	Oil %	Water %	Charcoal %	Gas %
400	42.55	6.01	42.03	35.05	22.40
425	44	7	37	34.99	21.01
450	50	12.80	34.73	32.16	20.03
475	54	16.33	33.20	30.76	19.07
500	55.70	20.53	34.33	27.60	17.10
525	56.56	25.56	33.63	26.66	16.12
550	55	17.53	34.10	27.03	20.33
575	53.30	17.13	34.20	26.50	21.02
600	51.13	17.13	34.60	26.20	22.06

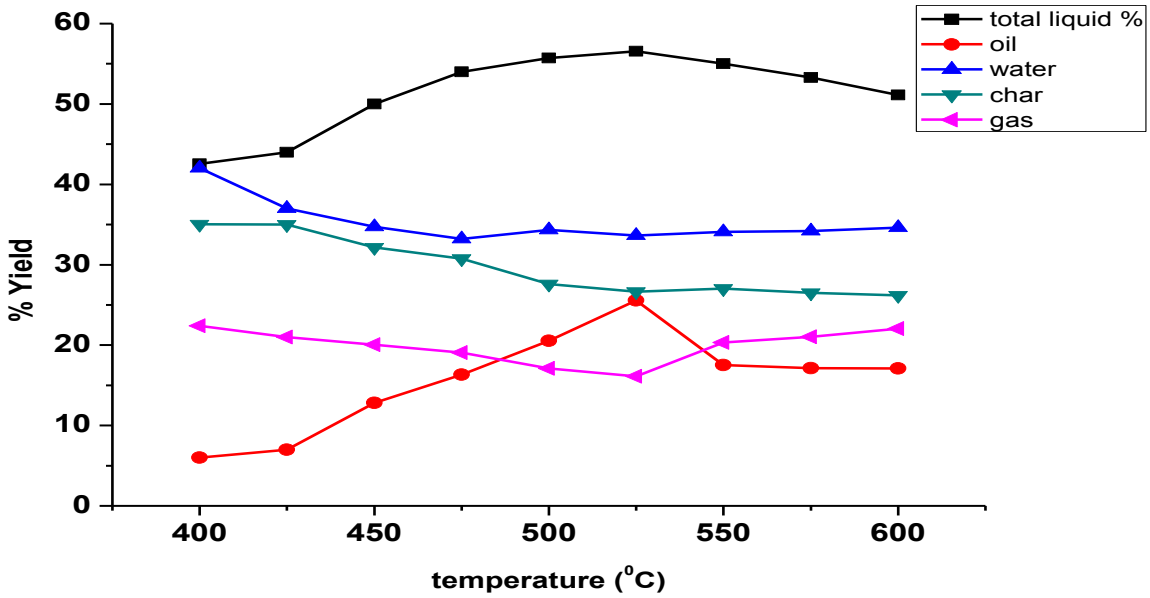


Figure 6: pyro-lytic yield of linseed de-oiled cake with temperature

5.3 Thermo gravimetric analysis and Kinetic study

Thermal behaviour of linseed cake can be improved by knowing thermal degradation kinetics. So the kinetic study of linseed cake pyrolysis provides a useful basis upon which to design a pyrolysis reactor. A thermo-gravimetric analysis (TGA) technique is an excellent way for studying the kinetics of thermal degradation. It provides information on pre-exponential factor and activation energy. When these polymeric materials subjected to heating or burning conditions, complicated reaction mechanism such as random-chain scission, end- scission, chain stripping, cross-linking and coke formation take place.

The mechanisms of pyrolysis include a wide range of different reactions. Not every reaction causes the release of a volatile molecule. Some only cause a change in mechanical properties. During thermo-gravimetric analysis, only the weight loss is measured on heating, that means only those reactions causing the weight loss are considered. Furthermore, because of the system complexity, all reactions are lumped together into an overall reaction.

5.3.1 Differential mass loss (DTG)

Differential mass loss (DTG) thermo grams of thermal decomposition of linseed cake pyrolysis, at three heating rates 10, 15, 20, K min^{-1} under inert atmosphere, are shown in Fig. 4. As expected three regions are evident which correspond to water evaporation, active and passive pyrolysis. The first region from 330 K to 380 K is related to the extraction of moisture and adsorbed water in the linseed cake sample.

The main pyrolysis process proceeds in a range from approximately 450 K to 650 K for low heating rate and 740 K for high heating rate. In this region (active pyrolysis), there are two peaks which the Literature shows to be related to hemicellulose and cellulose decomposition, while lignin is decomposed in both regions of active and passive pyrolysis without characteristic peaks.

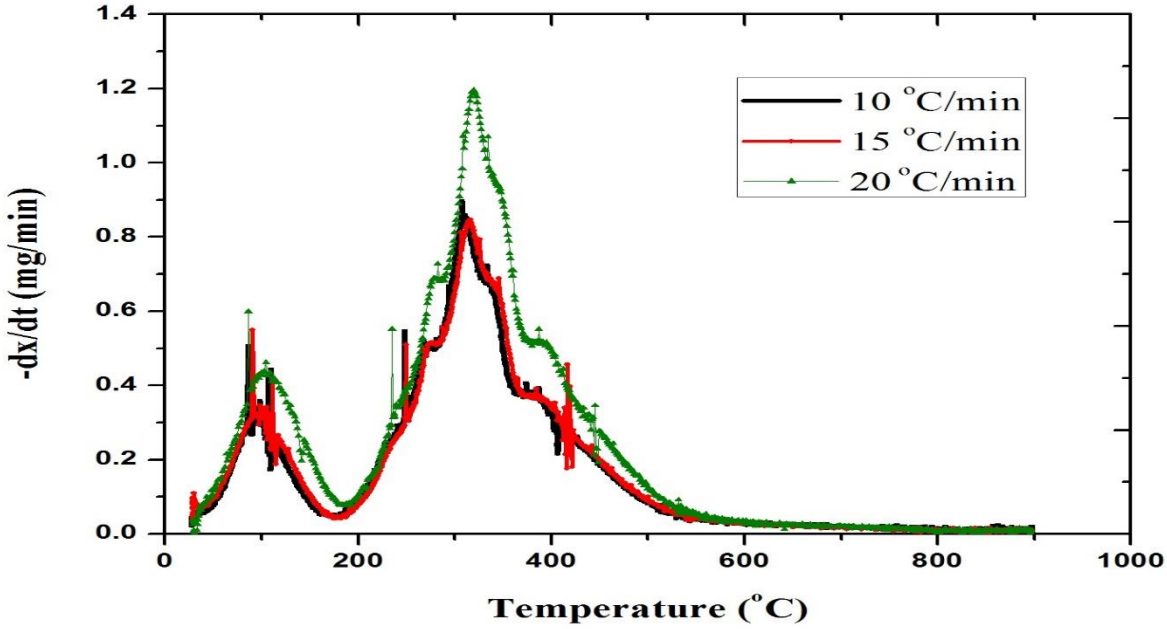


Figure 7: Differential mass loss (DTG) curve

5.3.2 The weight loss curve (TG)

The weight loss curve (TG) in Fig. 8 shows the loss of mass with temperature at different heating rates for linseed cake. As can be seen from the plot, the de-volatilization process begins at about 450 K and proceeds rapidly with increasing temperature until about 660 K and then the weight loss decreases slowly to the final temperature. The solid residue yields are about 28% for linseed cake.

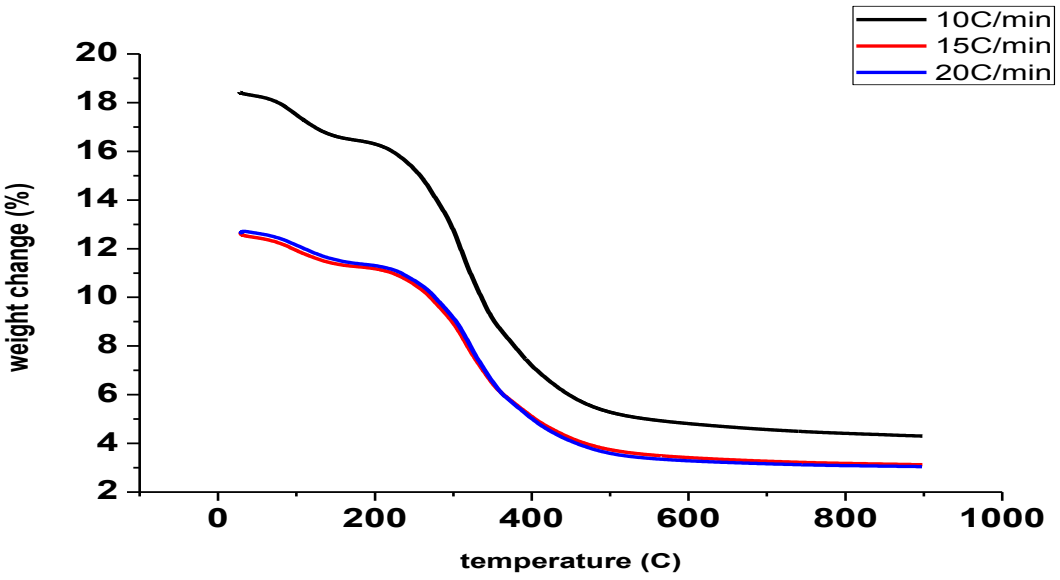


Figure 8: The weight loss curve (TG)

The effect of heating rate is shown in below figure. Heating rate affects TG curve positions, maximum decomposition rate and location of maximum Tm peaks. Fig. 4 shows DTG curves of linseed cake. When heating rate increases, starting and final temperature of active and passive pyrolysis region (Figs. 2 and 4) also increase.

The water evaporation region does not vary because the heating rate used for dehydration was identical for each analysis (Fig. 4). Maximum points of TG and minimum points of DTG curves are shifted towards higher temperature. This can be explained on the basis of heat transfer limitation.

During the analysis, at low heating rate, a larger instantaneous thermal energy is provided to the system and a longer time may be required for the purge gas to reach equilibrium with the temperature of the furnace of the sample. While at the same time and in the same temperature region a higher heating rate has a short reaction time and therefore the temperature needed for the sample to decompose is also higher.

5.4 Characterization of Raw Material and Bio-oil

5.4.1 Fourier transforms infrared spectroscopy (FTIR)

The oil was analysed using Fourier Transform Infrared spectroscopy (FT-IR).The FTIR spectra Were collected in the range of 400-4000 cm^{-1} region with 8 cm^{-1} resolution. The FTIR imaging is carried out using Perkin Elmer RX.

5.4.2 FT-IR analysis of linseed cake and linseed pyro-lytic oil

Fourier Transform Infrared (FT-IR) Spectroscopy is one of the important techniques which base its functionality on the principle that almost all molecules absorb infrared light. Only the monatomic (He, Ne, Ar, etc.) and homo-polar diatomic (H_2, N_2, O_2, etc.) molecules do not absorb infrared light. On interaction of an infrared light with oil, chemical bond will stretch, contract and absorb infrared radiation in a specific wave length range regardless structure of

the rest of the molecules. Based on this principle functional group present in the pyro-lytic oils were identified. The FT-IR spectrum for both the pyro-lytic oils is shown in Fig 4.4 and 4.5 and results from the transmittance spectrums are presented in Table 4.5 and Table 4.6. The data shows that the present oils contain mainly aliphatic and aromatic compounds.

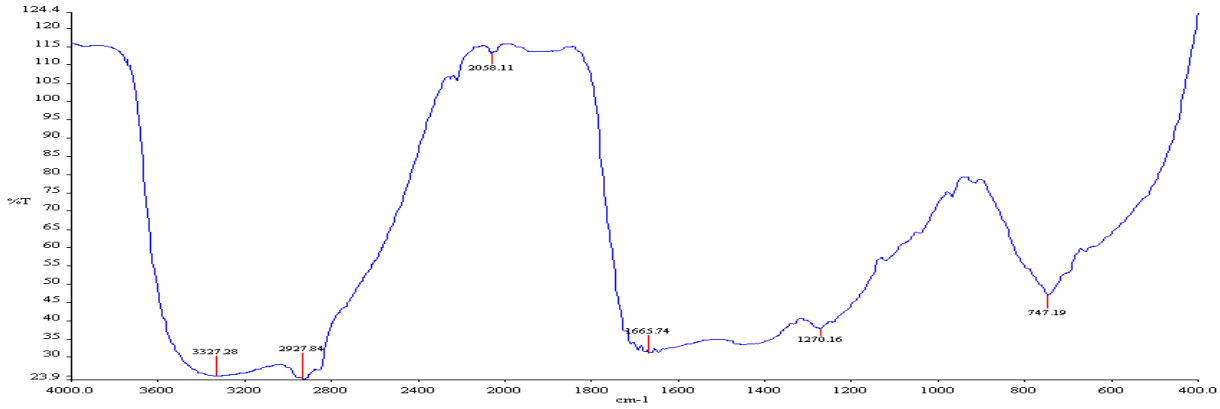


Figure 9: FTIR Analysis of Bio-mass

Table 10: **FTIR analysis of Bio-mass**

Compound Type	Frequency
O-H stretch by bonded alcohol	3327.28
C-H stretch alkanes	2927.84
C≡H stretch alkynes	2059.11
NO_2 asymmetrical stretching nitro compounds	1665.74
C-N stretch amines	1270.16
C-H bend phenyl ring substitution bonds	747.19

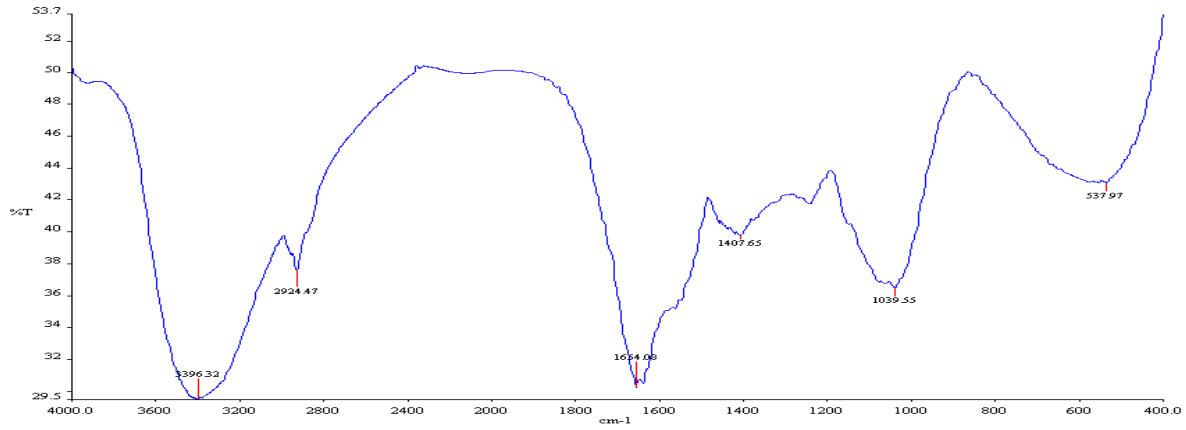


Figure 10: FTIR analysis of Bio-oil

Table 11: FTIR analysis of Bio-oil

Compound Type	Frequency
O-H stretch by bonded alcohol	3396.32
C-H stretch alkanes	2924.47
NO_2 asymmetrical stretching nitro compounds	1654.08
C-H scissoring and bending alkanes	1407.65
O-C stretch amides	1039.55

5.5 GC-MS analysis

The composition of oils were derived from linseed cake and tube pyrolysis was analysed using gas chromatography/mass spectrometry (GC/MS- QP 2010 SHIMADZU), equipped with flame ionization and mass spectrometry detection (GC-FID-MS). A capillary column coated with a 0.25 μm film of DB-5 with length of 30 m and diameter 0.25 mm was used. The GS was equipped with a split injector at 200 ^{0}C with a split ratio of 1:10. Helium gas of 99.95% purity was used as carrier gas at flow rate of 1.51 ml/min. The oven initial temperature was set to 700

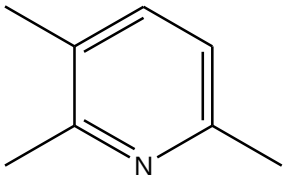
^{0}C for 2 min and then increased to 300 ^{0}C at a rate of 100 ^{0}C/min for 7 min. All the compounds were identified by means of the NIST library. Mass spectrometer was operated at an interface temperature of 240 ^{0}C with ion source temperature of 200 ^{0}C of range 40-1000 m/s.

Table 12: GC-Mass composition of the major compounds in Bio-oils from pyrolysis of linseed de-oiled cake.

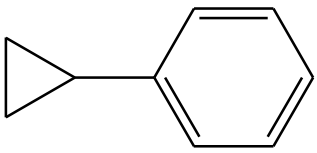
R. Time	Area%	Name of the compound	Molecular structure
5.339	0.50	Pyridine, 2, 3, 6-trymethyl	$C_8H_{11}N$
5.689	0.46	Cyclopropylbenzene	C_9H_{10}
6.795	2.22	Benzenemethanol	$C_8H_{10}O$
7.397	0.397	Benzoxazole	C_7H_5NO
8.051	1.07	Phenol, 4-ethyl	C_9H_9NO
8.341	0.81	1H-Pyrrole, 1-(2-furanylmethyl)	$C_8H_{16}O_5$
9.819	0.93	Phenol, 4-ethyl-2-dihydro-3-methyl	C_8H_9ON
10.294	1.11	2, 2, 5, 6-Tetramethyl-1, 3-oxathiane	$C_9H_{34}O_8$
11.074	1.18	3-Amino-4-methylbenzyl alcohol	C_8H_9ON
12.114	1.64	2, 3-Dimethyl-3H-1-benzazepine	$C_{16}H_{17}NO_5$
13.934	1.29	Hexadecane	$C_{16}H_{34}$
14.848	1.29	8-Heptadecene	$C_{17}H_{34}$
15.078	0.71	Heptadecane	C_3H_{36}
16.906	0.37	Pentadecanitrile	C_5H_9N
17.827	4.38	Hexadecanoic acid	$C_{16}H_{32}O_2$
19.580	28.0	cis-13-octadecatrienoic acid	$C_{18}H_{30}O_2$
20.858	0.61	Tridecane	$C_{13}H_{28}$
21.452	1.71	9-octadecenamide	$C_{18}H_{35}NO$

22.039	0.49	Thiocarbamic acid	$C_{13}H_{14}N_2O_3S_3$
23.993	0.50	1, 4-Bis (trimethylsilyl) benzene	$C_{12}H_{10}Si_2$
24.966	0.98	Isoindole-1, 3(2H)-Diane	$C_9H_7NO_2$
26.318	5.63	Cyclotrisiloxane, hexamethyl	$C_{12}H_{30}O_{21}$
27.818	0.59	5, 8-epoxy-15-nor-labdane	$C_5H_{35}N_3$
29.022	0.39	2-(dichloromethyl)-4-(4-methylphenyl	$C_{12}H_{11}Cl_2N_3O_2$
30.656	0.10	2-P-Nitrophenyl-1,3,4-Oxadiazol-5-One	$C_8H_5N_5O_4$

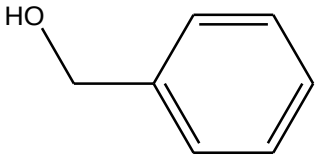
Table 13: GC-MS compound structures



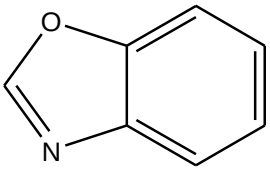
pyridine, 2, 3, 6-trimethyl



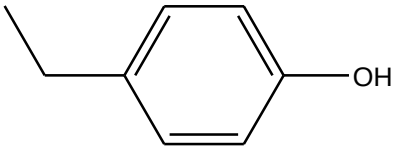
Cyclopropylbenzene



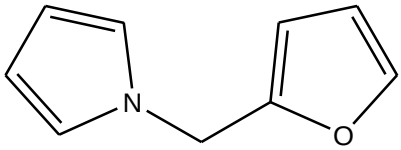
Benzenemethanol



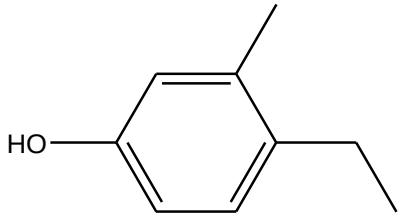
Benzoxazole



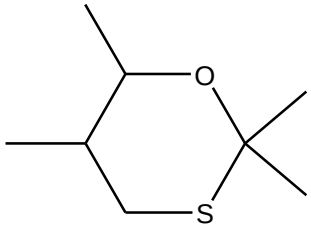
Phenol, 4-ethyl



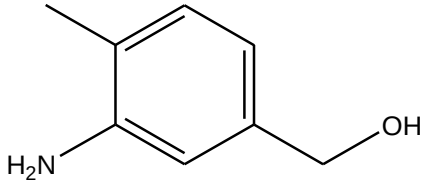
1H-Pyrrole, 1-(2-furanylmethyl)



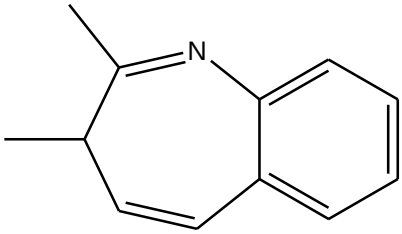
Phenol, 4-ethyl-2-dihydro-3-methyl



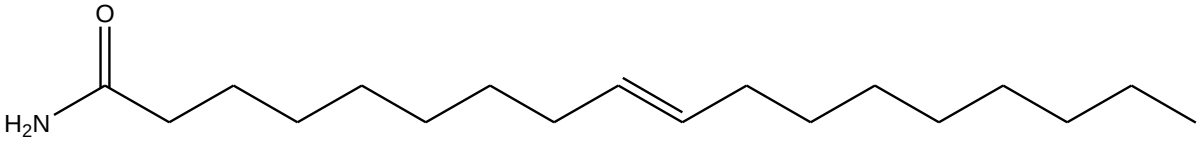
2, 2, 5, 6-Tetramethyl-1, 3-oxathiane



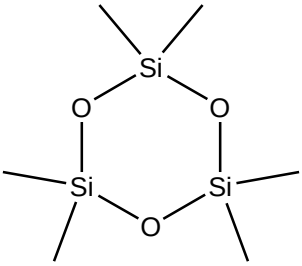
3-Amino-4-methylbenzyl alcohol



2, 3-Dimethyl-3H-1-benzazepine



9-octadecenamide



Cyclotrisiloxane, hexamethyl

5.6 Physical characteristics of pyro-lytic oil

Physical properties such as specific gravity, density, Kinematic viscosity, Conrad son carbon residue, flash point, fire point, pour point, cloud point, calorific value, sulphur content, distillation boiling range and cetane index of the linseed cake oil was determined using the standard methods, which is shown in the Table 5.

Table 14: Physical characteristics of pyro-lytic oil

Physical properties	Linseed pyro-lytic oil	Linseed seed
Kinetic viscosity @40 ^{0}C in	1.99	1.97
Density@15 ^{0}C in gm /cc	0.949	0.9301
Specific gravity@15 ^{0}C/15 ^{0}C	0.9298	0.9399
Flash point by Abel Method	26 ^{0}C	24 ^{0}C
Fire point by Abel Method	34 ^{0}C	32 ^{0}C
Cloud Point	25 ^{0}C	15 ^{0}C
Pour point	4 ^{0}C	4 ^{0}C
Conradson carbon Residue	1.99%	1.94%
Gross Calorific Value (cal/g)	7599	8094
Sulphur Content	0.20	0.20%
Cetane Index	31	31
Distillation		
Initial Boiling Point	90	90
Final Boiling Point	362	344

5.7 Soxhlet apparatus

Normally a solid material containing some of the desired compound is placed inside a thimble made from thick filter paper, which is loaded into the main chamber of the Soxhlet extractor. The extraction solvent to be used is taken into a distillation flask and the Soxhlet extractor is now placed onto this flask. The Soxhlet is then equipped with a condenser.

The solvent is heated to reflux. The solvent vapour travels up a distillation arm, and floods into the chamber housing the thimble of solid. The condenser ensures that any solvent vapour cools, and drips back down into the chamber housing the solid material.

Table 15: Soxhlet apparatus

Parameters	**weight (gram)**
Weight of the linseed cake	10.08
Weight of the thimble	2.48
Total weight	12.56
Weight of the extractor	10.99
Weight loss	1.57
% of oil extracted	14.50%

Chapter 6

Conclusion

Conclusion:

Conclusion and Future work:

Biomass pyrolysis has taken advantages because of an opportunity for the processing of agricultural residues, wood wastes and municipal solid waste into clean energy. This study focused on pyrolysis of de-oiled cake with different operating condition such as temperature, heating rate and time. The pyrolysis of de-oiled has been carried out in semi-batch reactor with different temperature range of (350-600^{o}C) to obtained the maximum yield of bio-oil. The following conclusion and recommendation has been drawn.

The pyrolysis process was started from 350^{o}C temperature on wards as it was selected based on the result obtained from thermo-gravimetric analysis of the linseed de-oiled cake.

Maximum yield of bio-oil was obtained (46.24%) at an optimum temperature of (525^{o}C) because of at this temperature secondary reaction such as (cracking, re-polymerization and re-condensation occurs to maximize the liquid yield.

The char yield decreases with increasing in temperature this occurs due to secondary de-composition of char at higher temperature causes the decrease in liquid yield while the gas and total conversion increases. With increase in temperature the gas yield increases due to the decomposition of oil vapours into permanent gases. From this we can estimate that temperature has significant effect on pyrolysis yields and conversion efficiencies.

The major functional group present in linseed de-oiled cake are alcohol, alkanes, alkynes and amines. Around 25 chemical compound is present in bio-oil of linseed cake which was obtained from GC-MS analysis, the major chemical compounds are benzene methanol, hexadecanoic acid cis-13-octadecatrienoic acid, 9-octadecenamide. After separation and analysis of these materials may contribute to major industrial applications.

Several physical properties investigation of bio-oil indicated that it desires up gradation to be used as alternative fuel.

Future work:

This work can be drawn out to develop on stabilization and up-gradating of bi-oil with some modification to equipment configuration before applying them in further industrial application. Also it is important to optimize the process by maximum product quality and quantity while paying proper attention to minimizing cost and environmental concerns.

Numerous catalyst have been developed and tested in pyrolysis process to improve the quality of bio-oil.

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